

## DESCRIPTION

## CURABLE COMPOSITION

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## TECHNICAL FIELD

This invention relates to curable compositions, which are particularly usable for coatings, comprising compounds containing activated unsaturated groups, compounds containing activated hydrogen atoms, tertiary alkyl phosphines and carboxylic acids. The compositions can be cured at low temperatures and show at the same time good storage stability at room temperature.

## BACKGROUND ART

15 Coating compositions containing activated unsaturated groups and activated hydrogen atoms are known, in general, from several references.

) An early example is German Patent No. DE-PS 835809, which discloses a process for production of products derived from 20 compounds containing activated hydrogen atoms, including activated methylene groups, and activated double bonds.

U.S. Patent No. 2,759,913 discloses a composition of the above type, which may be prepared at ambient and elevated temperatures. More specifically, the reference generally 25 describes the production of polymeric materials prepared from compounds containing at least two activated ethylenic double bonds and components containing at least two activated

5,017,649, are more soluble in organic coatings, but they also reduce the hydrolytic stability of the coatings. This is known from Journal of Coatings Technology, Vol. 61, No. 770, March 1989, page 89. The sensitivity of polyesters towards hydrolysis in the presence of strong alkaline catalysts was also described in a product information bulletin from Eastman Kodak Company: "The Utility of Acetoacetoxyethyl Methacrylate (AAEM) in Thermoset Coatings" (page 14, last section: "Michael addition").

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#### DISCLOSURE OF INVENTION

Therefore, the object of the present invention is to provide curable compositions, particularly usable for coatings, which can be crosslinked at low temperatures or room temperature but which are, on the other hand, also storage stable at room temperature, and which do not suffer from the drawbacks of strong basic catalysts, which may impart yellowing, cloudiness, and hydrolysis instability to the coating.

According to the invention, the object is achieved by the curable compositions of this invention which is:

A curable composition comprising:

- (i) a compound (A) having at least two unsaturated groups which are activated for Michael addition,
- 25 (ii) a compound (B) having at least two activated hydrogen atoms,
- (iii) a tertiary alkyl phosphine (C), and

liquid curable coating compositions, the number average molecular weight of the compound (B) having at least two activated hydrogen atoms should be preferably in the range between 230 and 2,000. For solid powder coating systems, the 5 number average molecular weight of the compound (B) having at least two activated hydrogen atoms could be preferably in the range between 1,000 and 40,000.

Compounds containing both malonate and acetoacetate groups in the same molecule are also suitable and can be 10 obtained, for example, by the Michael addition between a malonate functional polyester and an acetoacetate functional acrylic compound (e.g., acetoacetoxyethyl acrylate).

Additionally, simple mixtures of malonate and acetoacetate group-containing compounds are suitable as well. Low 15 molecular weight alkyl acetoacetates and malonates, such as ethyl acetoacetate and dimethyl malonate, may also be used as reactive diluents.

The compound (B), which includes the aforementioned and other malonate and/or acetoacetate group-containing compounds 20 and their methods of production, are generally known to those skilled in the art.

The tertiary alkyl phosphine (C) may be aliphatic, cycloaliphatic, or of mixed character.

Suitable examples include tributylphosphine, 25 triisobutylphosphine, tri-tertiary-butylphosphine, tris(2,4,4-trimethylpentyl)phosphine, tricyclopentylphosphine, tricyclohexylphosphine, tri-n-octylphosphine (TOP), tri-n-

**Dodecylphosphine.**

In contrast to aliphatic tertiary phosphines, aromatic tertiary phosphines show very low catalytic activity, if any.

From the viewpoint of handling, safety, and environmental properties (e.g., a low vapor pressure), tri-n-octylphosphine (TOP) and tri-n-dodecylphosphine are particularly preferable.

The aforementioned phosphines are commercially available or may be prepared according to standard methods of organic chemistry such as Grignard reaction of alkylhalogenides with

phosphorous trichloride or catalytic addition of alkenes to phosphane.

The carboxylic acid (D) represents compounds containing carboxylic acid groups.

5        Various carboxylic acids can be used in the curable compositions of this invention, which carboxylic acids can extend the pot-life of the mixture considerably and make them storage stable at ambient temperature. Among these, some carboxylic acids are preferred for the curing at elevated 10      temperatures above 100°C, such as formic acid, acetic acid, propionic acid, pentanoic acid, hexanoic acid, malonic acid, cyanoacetic acid, nitroacetic acid, phenylacetic acid,  $\alpha$ -oxoacetic acid, acrylic acid, methacrylic acid, maleic acid, succinic acid, and glyoxylic acid.

15       Preferred among them is a saturated fatty acid having a molecular weight of 80 or less, such as formic acid, acetic acid, or propionic acid, especially for curing at low temperatures below 100°C or even at room temperature.

The curable compositions of this invention are prepared 20      by blending, mixing, or dissolving the aforementioned compound (A), compound (B), tertiary alkyl phosphine (C), and carboxylic acid (D) at room temperature. Important is the sequence of the addition of compound (A), compound (B), tertiary alkyl phosphine (C), carboxylic acid (D). In 25      general, carboxylic acid (D) must be present in a system which is able to react (both components A+B are present) before the addition of tertiary alkyl phosphine (C).

Thus, a preferable method for the preparation of the curable composition comprises mixing compound (A), compound (B), tertiary alkyl phosphine (C), and carboxylic acid (D) in an arbitrary order with the proviso that tertiary alkyl phosphine (C) is added after the addition of carboxylic acid (D).

In a further embodiment, the mixture of tertiary alkyl phosphine (C) and carboxylic acid (D) is prepared separately and the mixture is then mixed with compound (A) and compound (B) in an arbitrary order.

After the addition of each component, the mixture is thoroughly stirred in order to finely disperse or dissolve the components in each other before the addition of the next component is processed. As mentioned above, the addition of tertiary alkyl phosphine (C) to a solution of (A+B) before adding carboxylic acid (D) may result in an immediate increase in viscosity and formation of gel particles, so that the curable coating composition can no longer be applied. The amount of tertiary alkyl phosphine (C) is 0.1-10% by weight, preferably 0.2-2.0% by weight of the total weight of the curable coating composition. The amount of carboxylic acid (D) depends on the amount of tertiary alkyl phosphine (C). The equivalent of the carboxylic acid groups of carboxylic acid (D) should exceed the equivalent of the phosphine compounds of tertiary alkyl phosphine (C). For good long term storage stability, the carboxylic acid group equivalent may be applied in an excess of at least 50%.

## EXAMPLES:

## Example 1

100 ml of toluene was sparged with nitrogen and heated to 5 90°C. Then, a solution of 60.0 g of methyl methacrylate, 20.0 g of butyl acrylate, 20.0 g of 2-acetoacetoxyethyl methacrylate, and 1.50 g of azobisisobutyronitril (AIBN) was dropped into hot toluene over 3 hours. Then, the mixture was stirred for another three hours. After cooling to room 10 temperature a viscous resin was obtained containing a copolymer having pendant acetoacetate groups, which represents compound (B), (molecular number average: Mn = 16,000; glass transition temperature: Tg = 38°C). To that resin, 30.0 g of trimethylolpropane triacrylate (compound (A)) was added and 15 dissolved followed by 0.7 g of formic acid (carboxylic acid (D)) and 2.0 g of trioctylphosphine (tertiary alkyl phosphine (C)). The mixture was adjusted with additional toluene until a coating viscosity of 200 mPas at 25°C was reached. The final curable coating composition was applied on top of an 20 aluminum specimen at a coating thickness of approximately 40 µm and cured under two different conditions at 75°C for 30 minutes and at 120°C for 30 minutes.

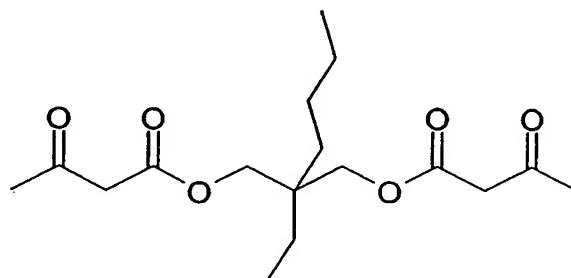
Solvent resistance <sup>1</sup> / Solvent resistance <sup>1</sup> /		Storage
Pencil hardness <sup>2</sup>	Pencil hardness <sup>2</sup>	Stability
(75°C/30 min)	(120°C/30 min)	at Room Temp.
50	>200	> 6 months
2H	3H	

<sup>1</sup>Solvent resistance of the hardened coating, tested by repeated rubbing of the film surface with a woodpulp cloth impregnated with methyl ethyl ketone (MEK). The number of rubbings that still did not produce any visible damage to the coating was measured.

<sup>2</sup>Pencil hardness (measured according to ASTM procedure D3363)

#### Examples 2-8

General procedure: 5.00 g of trimethylolpropane 10 triacrylate (compound (A)) was mixed with 5.00 g of the diacetoacetate (compound (B)),



which was prepared by transesterification of ethyl acetoacetate and 2-butyl-2-ethyl-1,3-propane diol. To that 15 mixture, 1.0 mmol of a carboxylic acid (carboxylic acid (D), see Table 1 below, column 3) was added and completely dissolved. Then, 0.5 mmol of a phosphine compound (tertiary alkyl phosphine (C), see Table 1 below, column 2) was added

Table 1:

Example	Tertiary alkyl phosphine (C)	Carboxylic acid (D)	Solvent resist. <sup>1</sup> / Pencil hardness <sup>2</sup> (25°C/ 7 days)	Solvent resist. <sup>1</sup> / Pencil hardness <sup>2</sup> (80°C/ 30 min)	Solvent resist. <sup>1</sup> / Pencil hardness <sup>2</sup> (140°C/ 20 min)	Storage Stability at Room Temp.
2	TOP	Formic acid	25 H	30 2H	>50 2H	>6 months
3	TCHP	Acetic acid	15 H	30 2H	50 2H	4 months
4	TOP	Malonic acid	no cure	3 H	10 2H	>6 months
5	TOP	Acetic acid	15 6B	40 H	> 50 2H	3 months
6	TCHP	Malonic acid	no cure	2 HB	8 2H	6 months
7	TCHP	Formic acid	30 H	40 2H	> 50 2H	> 6 months
8	TOP	Glyoxylic acid	no cure	39 H	>50 H	2 months

<sup>1</sup>Solvent resistance of the hardened coating, tested by repeated rubbing of the film surface with a woodpulp cloth impregnated with methyl ethyl ketone (MEK). The number of 5 rubbings that still did not produce any visible damage to the coating was measured.

<sup>2</sup>Pencil hardness (measured according to ASTM procedure D3363)

TOP = trioctylphosphine

TCHP = tricyclohexylphosphine

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### Examples 9-12

General procedure: 5.00 g of trimethylolpropane triacrylate (compound (A)) was mixed with 7.50 g of the oligomeric malonate depicted below (compound (B), molecular 15 weight ~1,000),

Table 2:

Example	Tertiary alkyl phosphine (C)	carboxylic acid (D)	Solvent resist. <sup>1</sup> /Pencil hardness <sup>2</sup> (100°C/30 min)	Solvent resist. <sup>1</sup> /Pencil hardness <sup>2</sup> (145°C/20 min)	Storage Stability at Room Temp.
9	TOP	Formic acid	25 H-B	>50 H-2H	6 months
10	TOP	Acetic acid	20 3B	40 H	4 months
11	TOP	Malonic acid	3 3B	50 H-2H	6 months
12	TOP	Glyoxylic acid	20 H	~ 50 2H	3 months

<sup>1</sup>Solvent resistance of the hardened coating, tested by repeated rubbing of the film surface with a woodpulp cloth impregnated with methyl ethyl ketone (MEK). The number of rubbings that still did not produce any visible damage to the coating was measured.

<sup>2</sup>Pencil hardness (measured according to ASTM procedure D3363)

#### INDUSTRIAL APPLICABILITY

10 The products of this invention are useful as coating materials or as materials to make binder components in varnishes, adhesives, paints, and printing inks.